

EXAFS Characterization of U(VI) Sorption Complexes on Clinoptilolite and Montmorillonite

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Beamline(s): X11A

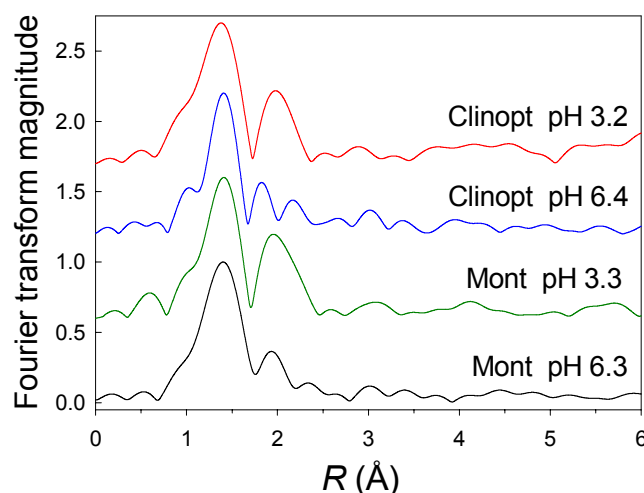
Introduction: Clinoptilolite and montmorillonite are important mineral constituents found at Yucca Mountain, NV, a proposed repository for high-level nuclear waste. Clinoptilolite is a zeolite mineral characterized by open intracrystalline channels parallel to the c-axis that allow easy movement of some ions and molecules into and out of the structure. Montmorillonite is a smectite clay with a 2:1 layered structure, characterized by a layer of octahedrally coordinated Al atoms sandwiched between two layers of tetrahedrally coordinated Si atoms. Both minerals contain two types of sorption sites: (i) permanently charged cation-exchange sites and (ii) variably charged surface hydroxyl groups. An understanding of the mechanisms of U(VI) uptake by these minerals is important for prediction of radionuclide transport behavior.

Methods and Materials: Uranium L₃- and L₂-edge EXAFS spectroscopy was used to determine the structure of U(VI) species sorbed onto clinoptilolite and montmorillonite at solution pH ~3 and ~6 so the effect of pH on the sorption mechanism could be evaluated. UO₂²⁺-equilibrated suspensions of the solids were centrifuged to recover moist pastes, which were loaded into sealed holders for data collection at beamline X-11A. Uranium L₃- or L₂-edge fluorescence spectra were collected at room temperature using a 13 element detector.

Results: Fourier transform magnitudes (figure) are dominated by the U-Oaxial peak (characteristic of the linear O=U=O unit) and weaker peaks from the equatorial coordination. Comparison of the FTs reveal a difference in the equatorial coordination of the uranyl surface species as a function of pH for both minerals. Split equatorial shells are evident for both samples at pH ~6, whereas primarily a single shell exists at pH ~3. The split equatorial shells probably indicate that discrete equatorial oxygens form chemical bonds at surface functional groups, as would be expected for an inner-sphere-type surface complex. In contrast, the single equatorial shell for samples at pH ~3 suggests a more uniform equatorial bonding environment for the oxygens, as would be expected for an outer-sphere-type complex. Such an environment is consistent with ion exchange at cation-exchange sites of the sorbents. The findings for montmorillonite are consistent with results reported by Sylwester et al. (2000).

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References: E.R. Sylwester, E.A. Hudson, and P.G. Allen, "The structure of uranium(VI) sorption complexes on silica, alumina, and montmorillonite," *Geochim. Cosmochim. Acta*, **64**, 2431, 2000.



Fourier transform magnitudes for U(VI) sorbed on clinoptilolite and montmorillonite at different solution pH values.